**High-performance membrane electrode assembly with multi-functional
Pt/SnO₂-SiO₂/C catalyst for proton exchange membrane fuel cell operated under
low-humidity conditions**

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Abstract: A novel self-humidifying membrane electrode assembly (MEA) with homemade multi-functional Pt/SnO₂-SiO₂/C as the anode was developed to improve the performance of a proton exchange membrane fuel cell under low humidity. The MEAs' performance was evaluated at various temperatures and relative humidity levels. One MEA with a Pt/SnO₂-SiO₂/C anode catalyst achieved excellent low-humidity performance at a cell temperature of up to 60°C: the current density reached 600 mA cm⁻² at 0.7 V and 1050 mA cm⁻² at 0.6 V with 10% RH; after 96 h of continuous operation under the same conditions, the current density decreased by only 16% (to ~880 mA cm⁻²), whereas the current density of an MEA with JM Pt/C as the anode degraded by more than 60% within 10 h. The contact angle of the Pt/SnO₂-SiO₂/C anode was much lower than that of the Pt/C anode, indicating the

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former's excellent wettability. The high performance of the MEA with the Pt/SnO₂-SiO₂/C anode is attributable to the wettability of the doped binary oxide, especially of silicon oxide, and the promotion of tin oxide, which caused an interaction between the Pt and the oxide, resulting in enhanced performance under low humidification.

Keywords: Proton exchange membrane fuel cell; Membrane electrode assembly; Silicon and tin oxides; Low humidification

1. Introduction

Proton exchange membrane fuel cells (PEMFCs), with their high power density and efficiency and their environmental neutrality, are efficient power sources for electric vehicles and residential cogeneration systems [1-2]. In general, the performance of a PEMFC relies on the humidity of the membrane electrode assembly (MEA), since the proton conductivity of a Nafion membrane is a linear function of the MEA's water content; both the Nafion membrane and the Nafion in the catalyst layer (CL) should be sufficiently hydrated to achieve high proton conductivity [3-4]. To ensure adequate MEA hydration, water is frequently introduced into the cell via pre-humidified air and hydrogen fuel. However, this additional humidification also induces problems and lowers the cell's energy efficiency.

In response to this challenge, significant attention has been focused on the development of self-humidifying, high-durability, high-performance MEAs to simplify the auxiliary systems (in this case, by eliminating the humidification system). One method is to prepare a self-humidifying membrane using a mixture of inorganic oxide powder and Nafion solution [5-8]. The hygroscopic materials acted as water absorbers and thereby improved proton conductivity by keeping the membrane well hydrated under conditions of low or no humidity. Another approach is to fabricate a self-humidifying composite catalyst with a hygroscopic material [9-16]. Inoue et al. [9] created a SiO₂-containing CL by the hydrolysis/condensation of SiO₂ sol and catalyst ink. An MEA using SiO₂ CLs for both the anode and the cathode exhibited high low-humidity performance; at a cell temperature of 80°C and 30% RH for anode and

cathode, the current density at 0.7 V was 2.7 times larger than without SiO₂; however, they did not carry out a durability test. Su et al. [10] developed a Pt/SiO₂/C self-humidifying composite catalyst by introducing amorphous SiO₂ into the catalyst. Their MEA with a Pt/SiO₂/C anode catalyst exhibited excellent low-humidity performance and durability at a cell temperature of 50°C and with 28% RH for both anode and cathode; the current density at 0.6 V remained stable at 650 mA cm⁻² after 120 h of testing. Our group also prepared a Pt/RuO₂-SiO₂/C self-humidifying catalyst [11-12]. The self-humidification performance of an MEA prepared with Pt/RuO₂-SiO₂/C was further enhanced by the addition of ruthenium oxide; after 48 h of testing, the current density at 0.6 V remained stable at 700 mA cm⁻² in the absence of external gas humidification and at 50°C. Although the MEA showed good humidification performance and excellent long-term stability, the low-humidity performance of Pt/SiO₂-RuO₂/C decreased sharply as the cell temperature increased from 50 to 70°C. Hence, there is still considerable room for improvement in terms of low-humidity performance and durability in practical applications, because PEMFCs typically are operated at 60°C and above.

Recently, our group [17] prepared a Pt/SnO₂-SiO₂/C catalyst by using a binary oxide-modified carbon support on which Pt nanoparticles (NPs) were deposited to improve both activity and stability/durability. Interestingly, this catalyst exhibited not only significantly improved activity and stability/durability but also good wetting properties. Encouraged by this result, we attempted to fabricate MEAs with a Pt/SnO₂-SiO₂/C composite catalyst as the anode, and investigated their performance

and durability under low humidity and elevated temperature. As we expected, these MEAs exhibited excellent self-humidification performance, even up to 65°C.

2. Experimental

2.1. Preparation and characterization of Pt/SnO₂-SiO₂/C composite catalysts

The preparation of Pt/SnO₂-SiO₂/C was almost the same as previously reported by our group [11]. First, carbon black (XC72R) was pre-treated in a mixture of hydrogen peroxide and nitric acid, and then impregnated with either a mixture of tetraethyl orthosilicate (TEOS) and SnCl₄ in ethanol or TEOS alone in ethanol solution, under stirring at room temperature. Next, the system was placed in an oil bath at 70°C to evaporate the solvent and induce hydrolysis of the TEOS and SnCl₄. This was followed by calcining at 300°C in a nitrogen environment for 3 h to improve the bonding of silica tin oxide to the carbon support surface. Finally, Pt/SnO₂-SiO₂/C catalysts were prepared via an organic colloid method reported previously by our group [17]. The theoretical Pt loading of the catalysts was 20 wt%; we did not otherwise measure the Pt or oxide loadings.

A series of Pt/SnO₂-SiO₂/C catalysts was prepared in this work, which we denote as PSSC0, PSSC2, PSSC4, and PSSC6, the number indicating the mass percentage of tin oxide in the catalyst. For example, PSS4 denotes Pt/SnO₂-SiO₂/C with a tin oxide loading of 4.0 wt%. For all catalyst samples, the silica content was 6.0 wt%.

2.2. Preparation of MEAs

All MEAs had an active area of 5 cm² and were prepared using the catalyst

sprayed membrane method developed in our laboratory[18]. Before spray deposition of the catalyst layers, Nafion 212 membranes (DuPont, USA) were pre-treated using the same procedure: (i) treated with a 5 wt% H₂O₂ solution at 80°C for 1 h, (ii) treated in deionized water at 80°C for 1 h, (iii) treated with 0.5 M H₂SO₄ solution at 80°C for 1 h, and (iv) treated with deionized water at 80°C for 1 h. Anode catalyst inks were prepared by mixing homemade Pt/SiO₂/C or Pt/SnO₂-SiO₂/C catalyst, isopropanol, and 5 wt% Nafion solution (DuPont, USA). The cathode catalyst ink was prepared by the same method but with commercial Hispec 4100 Pt/C catalyst (40 wt% Pt, Johnson Matthey (JM)). The Pt loadings at the anode and cathode were 0.1 and 0.2 mg cm⁻², respectively, and the dry Nafion content in the anode and cathode CLs was adjusted to 25 wt%. For comparison, one MEA was prepared using JM Pt/C catalyst at both the anode and the cathode. The detailed compositions of these MEAs are provided in Table 1.

The hydrophilic properties of the MEAs were evaluated using the contact angle, which is commonly measured by the sessile drop method [19]. The measurements were performed with an OCA 40 Video-Based Automatic Contact Angle Meter (Dataphysics, Germany).

2.3. Single cell tests

A MEA was assembled with a catalyst-coated membrane and two GDLs without hot pressing, and performance testing was carried out in a standard single cell with an active area of 5 cm², using a Fuel Cell Testing System (Arbin Instruments, USA). Pure hydrogen and compressed air were fed to the anode and cathode, respectively, at

flow rates of 200 (hydrogen) and 550 mL min⁻¹ (air). Before the performance test, the cells were activated in a continuous discharge mode until stable performance was obtained; the activation was processed at a cell temperature of 70°C and with 100% RH for the hydrogen and air. The self-humidification performance measurements were carried out at various cell temperatures and RHs. And the RHs were calculated with the method reported by literature previously [20-21]. The back pressures of both hydrogen and air were 30 psi. The temperatures of the gas lines to the anode and the cathode were always set at 5°C above the humidification temperature to prevent water condensation.

2.4. Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) was used to study the polarization resistance of the MEAs, with a Zahner IM6e electrochemistry station (Zahner, Germany). These measurements were carried out at a cell potential of 0.8 V with an amplitude of 5 mV, and in the frequency range of 0.1 Hz to 1 kHz.

3. Results and discussion

3.1. Low-humidity performance of the MEAs

Fig. 1(a) compares the low-humidity performance of three MEAs with three different anode catalysts: MEA PSC with 6 wt% silica, MEA PSSC4 with 6 wt% silica and 4 wt% tin oxide, and the blank MEA JM Pt/C. MEA PSSC4 exhibited the highest low-humidity performance and stability at 60°C and 10% RH: the current density at 0.6 V reached 1050 mA cm⁻² and remained stable at 970 mA cm⁻² after 20 h of operation, implying that adding tin oxide and silica to the anode catalyst can yield

high and stable self-humidification. With the MEA PSC, the current density at 0.6 V remained stable at 800 mA cm^{-2} for 18 h but then rapidly decreased, similar to what we found in a previous study [10]. In contrast, the performance of MEA JM Pt/C decreased rapidly from 600 mA cm^{-2} to 200 mA cm^{-2} within 10 h, indicating this MEA had no self-humidification ability. Evidently, the MEA containing both tin oxide and silica in the anode catalyst demonstrated much better performance than the MEA containing only silica (PSSC0) and the MEA with no oxides.

Numerous researchers [10, 13-14] have previously reported the excellent self-humidification of silicon oxide-modified catalyst anodes at low or no humidity, but the self-humidification performance of the MEA was degraded quickly at a high cell temperature (such as 60°C and above). However; the further additions of tin oxide make it possible for self-humidifying MEAs to be applied at higher temperature. We believe that the good low humidity performance of MEA PSSC4 mainly benefits from the wettability of binary oxide and stability of the composite catalyst. The silica may function as a water uptake material to keep the anode layer and membrane wet, and the addition of tin oxide further enhances the MEA's wettability and stability, and boosts the oxygen reduction reaction (ORR) or the ethanol oxidation reaction, as has been recognized and reported by several groups [22-25].

We also conducted a long-term low-humidity test of the MEA PSSC4, the results of which are presented in Fig. 1(b). The current density remained constant at 880 mA cm^{-2} after 96 h of testing, showing only a slight decay in performance (16%, from an initial current density of 1050 mA cm^{-2}). These results confirm the excellent

performance of the MEA prepared using our homemade composite catalysts without any external humidification.

3.2. Wettability of the anode catalyst layers

According to previous reports, the wettability of the anode CL plays an important role in the performance of PEMFCs at low or no humidity, since the proton transport capacity of the Nafion membrane and the Nafion ionomer in the CL is greatly dependent upon water available in the membrane and CL [26]. To verify that the CL's hydrophilicity improved through the addition of silica and tin oxide, we measured the contact angle of the anode CL for all of the MEAs prepared in this study; these values are presented in Fig. 2. The contact angle of the anode CL prepared with JM Pt/C catalyst reached 139.2° , whereas that of the MEA with a silica-containing catalyst as the anode was 127.3° , indicating that the addition of silica enhanced the CL's wettability. This result is consistent with previous reports' findings [10].

It is interesting that the further addition of tin oxide after silica was added clearly decreased the contact angle. The contact angles of MEAs with various amounts of tin oxide decreased with the increase in tin oxide content, indicating that tin oxide not only improved the catalysts' ORR performance but also enhanced the MEAs' wettability.

3.3. The effect of tin oxide content in Pt/SnO₂-SiO₂/C anode catalysts on MEA performance

Fig. 3 plots the performance of MEAs with various Pt/SnO₂-SiO₂/C anode catalysts (a) and their corresponding impedance spectra (b), at 60°C and full humidity

for both cathode and anode. Fig. 3(a) shows that, under fully humidified conditions, the performance results of the MEAs containing different amounts of tin oxide were comparable, and the current density at 0.7 V was over 600 mA cm^{-2} . The MEA PSSC4 (with 4 wt% SnO_2) achieved the best performance, with a slightly higher current density of 700 mA cm^{-2} at 0.7 V and 1050 mA cm^{-2} at 0.6 V. The MEA PSSC0 exhibited almost the same performance as the JM Pt/C MEA throughout the current density region, which corresponds with previous reports [10, 12]; meanwhile, the MEA PSSC6 (with 6 wt% SnO_2) showed slightly inferior performance due to excessive tin oxide in the composite catalyst.

These findings revealed that doping with an appropriate amount of tin oxide further improved cell performance under full humidity. Two factors may account for this: (i) the addition of tin oxide enhances both the water balance between the membrane and the CL and the wettability of the anode CL, which helps with the back-diffusion of water from cathode to anode, then facilitates the release of water from the cathode and thereby prevents cathode flooding; (ii) tin oxide boosts Pt activity [27].

Fig. 3(b) shows the in situ impedance curves of the five MEAs at a cell voltage of 0.8 V. The intercept of the semicircle at high frequency may be attributable to cell resistance (R_Ω) and charge transfer resistance (R_{ct}), as indicated by the diameter of the arc [28]. There is no significant difference in the ohmic resistance (R_Ω) between MEA JM PC, MEA PSSC0, MEA PSSC2, and MEA PSSC4; however, the R_Ω and R_{ct} of the MEA PSSC6 are higher than those of the other MEAs. In accordance with the cell

performance discussed earlier, this may be because the electrochemical characteristics of the CL were affected by the addition of excessive tin oxide. From these results we can conclude that the addition of an appropriate amount of tin oxide had no negative effect on the MEAs' fully humidified performance and in fact significantly enhanced their performance in the higher current region.

Fig. 4(a) shows the polarization curves of MEAs with various tin oxide loadings in the anode CL, operating at a cell temperature of 60°C and 10% RH. The MEAs containing tin oxide exhibited higher performance as the amount of tin oxide increased from 0 to 4 wt%; the current density at 0.7 V rose from 300 to 600 mA cm⁻² and the maximum power density from 630 to 760 mW cm⁻². However, further increasing the tin oxide content to 6.0 wt% had a negative impact: the current density at 0.7 V was only 200 mA cm⁻², and the maximum power density was 680 mW cm⁻². These results were consistent with those achieved at full humidification. As expected, the MEA JM PC exhibited the poorest performance at low humidification for both anode and cathode gases. For clarity, we plotted the MEAs' current densities at 0.7 and 0.6 V (see Fig. 4 (b)). Notably, adding hydrophilic silica and tin oxide to the anode CL greatly improved the MEAs' performance under low-humidity conditions. The MEA PSSC4 demonstrated the best performance—a current density of 600 mA cm⁻² at 0.7 V, which was 3.3 times that of the MEA JM PC (180 mA cm⁻²)—while the performance of the MEA PSSC6 decreased slightly. These results explicitly indicate that adding a suitable amount of hydrophilic tin oxide to the anode may be an ideal way to further realize non-humidified PEMFC operation.

3.4. The effect of cell temperature on MEA performance

Fig. 5 plots the effects of cell temperature on the performance of the MEA PSSC4 at 10% RH. As shown in Fig. 5(a), the performance decreased steeply in the low current density region; however, it improved to some extent at higher current densities as the cell temperature increased from 60 to 70°C (see Fig. 5(b)). This could have resulted from the increased amount of water generated at elevated current densities, which led to greater back-diffusion of water and enhanced MEA hydration due to the presence of hydrophilic silica and tin oxide in the anode. The optimal cell temperature for the MEA PSSC4 seemed to be 60°C, a conclusion supported by the consistent test results presented in Fig. 5(b). The current density of the MEA PSSC4 at 0.6 V remained stable at 980 mA cm⁻² at a cell temperature of 60°C, demonstrating favorable performance and stability. Notably, at 65°C, the current density of the MEA PSSC4 decreased only slightly, from 990 to 900 mA cm⁻², after 10 h of testing, another indication of good performance and stability. However, when the temperature reached 70°C, the performance decreased sharply from 900 to 180 mA cm⁻², possibly because water generated at the cathode was quickly lost to evaporation, leading to severe MEA dehydration at high temperature, especially with low or no humidity [29]. These results indicate that the MEA with hydrophilic silica and tin oxide in the anode was effective in maintaining consistent cell performance with no humidity in the temperature range of 60–65°C.

The operating temperature of PEMFCs is generally in the range of 60–80°C, so making self-humidifying MEAs that work at such temperatures is very important for

the practical application of this type of MEA. However, self-humidifying MEAs are temperature sensitive, and higher operating temperatures can make water retention at the anode CL very difficult. Indeed, the performance of MEA PSSC4 decreased quickly as the temperature reached 70°C.

3.5. Characterization of the Pt/SnO₂-SiO₂/C catalyst and the MEAs

Fig. 6 (a) and (b) present the TEM images of Pt/SnO₂-SiO₂/C with 4 wt% tin oxide (PSSC4). The active components were highly dispersed in the support, and the average Pt particle size was approximately 2–3 nm. No diffraction peaks associated with SiO₂ or SnO₂ could be observed, the oxides should be existed at the surface of the catalyst as amorphous film. These results are in agreement with our previous studies [10-11, 16]. Fig. 6(c) and (d) show the SEM images of the surfaces of the MEA JM PC and MEA PSSC4. There was no difference between the two samples; the JM Pt/C catalyst and PSSC4 composite catalyst were well connected with the Nafion ionomer and uniformly dispersed on the membranes to form porous catalyst layers. Fig. 6(e) and (f) show the cross-sectional morphology of the MEA JM PC and MEA PSSC4 in the anode. Evidently, the thickness of the anode CL with MEA PSSC4 (8.6 μm) is about twice that of MEA JM PC (4.4 μm), due to the CLs' different Pt contents (JM Pt/C, 40 wt%; Pt/SiO₂-SnO₂/C, 20 wt%). According to the EIS results, this difference in thickness had no influence on cell resistance, which is in accordance with our previous report [10, 17].

4. Conclusions

A new type of self-humidifying MEA was successfully fabricated using

homemade Pt/SnO₂-SiO₂/C as the anode. The catalyst was prepared by doping binary oxide on the carbon support, then adding Pt nanoparticles to this modified support via a colloidal method. Contact angle measurements revealed that an MEA prepared with Pt/SnO₂-SiO₂/C as the anode improved the wettability of the CL. An MEA with this binary oxide-modified catalyst as the anode exhibited much better low-humidity performance than an MEA with only a silica-modified catalyst as the anode, confirming the further improvement brought about by tin oxide. The optimal MEA had an anode catalyst containing 4 wt% SnO₂ and 6 wt% SiO₂. Its current density at 0.7 and 0.6 V reached 600 and 1050 mA cm⁻², respectively, at a cell temperature of 60°C and 10% RH for both anode and cathode gases. After 96 h of long-term testing under the same conditions, its current density remained at 880 mA cm⁻². Significantly, the operation temperature for the optimal MEA could be up to 65°C, indicating the excellent effect of adding tin oxide. We suggest that the enhancement by tin oxide may be attributable to two factors: (i) improved wettability due to the addition of tin oxide along with silica; and (ii) tin oxide's boosting of Pt activity.

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Table 1. Comparison of MEAs (Nafion content: 25 wt%)

MEA	Cathode (0.2 mg _{Pt} cm ⁻²)	Anode (0.1 mg _{Pt} cm ⁻²)
MEA JM PC	JM 40 wt% Pt/C	JM 40 wt% Pt/C
MEA PSSC0	JM 40 wt% Pt/C	Pt/SiO ₂ /C (6 wt% SiO ₂)
MEA PSSC2	JM 40 wt% Pt/C	Pt/SnO ₂ -SiO ₂ /C (2 wt% SnO ₂ , 6 wt% SiO ₂ , 20 wt% Pt/C)
MEA PSSC4	JM 40 wt% Pt/C	Pt/SnO ₂ -SiO ₂ /C (4 wt% SnO ₂ , 6 wt% SiO ₂ , 20 wt% Pt/C)
MEA PSSC6	JM 40 wt% Pt/C	Pt/SnO ₂ -SiO ₂ /C (6 wt% SnO ₂ , 6 wt% SiO ₂ , 20 wt% Pt/C)

Fig. 1 Constant voltage discharge performance at 0.6 V for 20 h for the three MEAs (a), and the long-term discharge curve of MEA PSSC4 (b), all at 10% RH for both anode and cathode. Cell temperature was 60°C; back pressure for both air and hydrogen was 30 psi; hydrogen and air flow rates were 200 and 550 mL min⁻¹, respectively.

Fig. 2 Contact angles of MEAs, measured by water droplet.

Fig. 3 Performance of MEAs with different anode catalysts at 100% RH (a), and in situ impedance curves of single cells at 0.8 V (b); the cell temperature was 60°C, and the back pressure for air and hydrogen was 30 psi.

Fig. 4 (a) Performance of MEAs with different anode catalysts operated at 60°C and 30 psi back pressure, with 10% RH at both anode and cathode; (b) current density of MEAs at 0.6 and 0.7 V.

Fig. 5 Polarization curves and power outputs (a) and constant voltage discharge performance (b)

of the PSSC4 MEA operated at different cell temperatures and 10% RH for both anode and cathode, and at a back pressure of 30 psi for anode and cathode.

Fig. 6 TEM images of PSSC4 (a, b); SEM images of surfaces and cross-sections of the MEA JM PC (c, d) and the MEA PSSC4 (e, f).

Graphical abstract

The MEA prepared by home-made multi-functional Pt/SnO₂-SiO₂/C as the anode catalyst exhibits high and stable self-humidification performance at cell temperature of 60°C and 10% relative humidity, the current density at 0.6 V can be up to 1050 mA cm⁻² and stable at 880 mA cm⁻² after 96 hours continuous running, with the degradation of 16%, which is much better than that of the blank MEA without insertion.